Phase Evolution and Stability of Aluminum Titanate Prepared by Solid-State Route and Solution Combustion Route

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By

VIDISHA SINGH (111CR0111)

Supervisor: Prof. Ranabrata Mazumdar

Department of Ceramic Engineering

National Institute of Technology, Rourkela, Odisha – 769008

Declaration

I hereby declare that the work presented in the thesis entitled "PHASE EVOLUTION AND STABILITY OF ALUMINUM TITANATE PREPARED BY SOLID-STATE ROUTE AND SOLUTION COMBUSTION ROUTE" submitted for B.Tech Degree to the National Institute of Technology, Rourkela has been carried out by me at Department of Ceramic Engineering, National Institute of Technology, Rourkela under the supervision of Dr. Ranabrata Mazumder. The work is original and has not been submitted in part or full by me for any degree or diploma to this or any other University/Institute.

VIDISHA SINGH

Roll No. – 111CR0111

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VIDISHA SINGH (111CR0111)

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008, ODISHA, INDIA

Certificate of Approval

This is to certify that the thesis entitled "**PHASE EVOLUTION AND STABILITY OF ALUMINUM TITANATE PREPARED BY SOLID-STATE ROUTE AND SOLUTION COMBUSTION ROUTE**" submitted to the National Institute of Technology, Rourkela by **VIDISHA SINGH (111CR0111)** for the award of the Degree of Bachelor of Technology in Ceramic Engineering is a record of bonafide research work carried out by her under my supervision and guidance. The results presented in this thesis has not been submitted to any other University or Institute for the award of any degree or diploma. The thesis, in my opinion, has reached the standards fulfilling the requirement for the award of the degree of Bachelor of technology in accordance with regulations of the Institute.

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Prof. Ranabrata Mazumdar

Department of Ceramic Engineering

National Institute of Technology, Rourkela

Date:

ABSTRACT

Aluminum titanate (Al_2TiO_5) powder was synthesized using two different route, namely, solid-state route and solution combustion route. In solid-state route, two different types (micron and nano-size powder) of Al_2O_3 precursor powder was used. Phase evolution and powder morphology were investigated by X-ray diffraction method and Field emission scanning electron microscope (FESEM) respectively. In case of large particle Al_2O_3 precursor powder, Al_2TiO_5 (AT) phase was formed at 1500^{o}C with a yield of 97%. Whereas using nano-Al_2O_3 precursor powder, AT phase was formed at 1350^{o}C with a yield of 91% and almost phase pure powder can be prepared at 1500^{o}C. Average particle size of the AT powder was 11 μm (using large particle Al_2O_3) and 10.2 μm (using nano-size Al_2O_3) for calcination at 1500^{o}C. AT powder was also synthesized by citrate-nitrate solution combustion method. The molar ratio of metal (Al:Ti) and citric acid was varied to get a uniform and complete combustion. A significant amount Al_2TiO_5 phase was formed at 1350°C. The stability of the solid state route prepared AT powder was investigated by keeping the powder at 1150°C/6hr. It was observed from the XRD analysis that only 40% AT-phase was retained in samples prepared with micron size Al_2O_3, but, in case of sample prepared using nano size Al_2O_3, 93% AT-phase was retained.

Keywords: Al_2TiO_5; Solid state route; Solution combustion route; Nanoparticle;

List of Contents

List of Figures

1. INTRODUCTION

Composites of alumina-titania are used for thermal barrier coating applications due to its high emissivity [1]. In Al_2O_3–TiO_2 system, Aluminum titanate (Al_2TiO_5) possess excellent thermal shock resistance and a relatively low thermal expansion coefficient ($1x10^{-6}°C^{-1}$) and its melting point is 1860 °C. Al_2TiO_5 (AT) is thermodynamically stable only above a temperature of 1280 °C, up to its eutectoid point. Below 1280°C, the metastable compound (Al_2TiO_5) undergoes a eutectoid decomposition that results in formation of α-Al_2O_3 and TiO_2 (rutile) [2]. The decomposition starts around 900°C and it is generally seen that the rate of decomposition is maximum at a temperature of 1100°C. The decomposition usually starts when the adjacent Ti^{4+} (0.67 Å) and Al^{3+} (0.54 Å) undergo octahedral collapse because the lattice site occupied by the Al^{3+} ions is too large [3]. Energy (thermal) released from this collapse allows $Al^{3+}$to shift and move from its position and causes structural dissolution to corundum (Al_2O_3) and rutile (TiO_2). The application of this compound in the engineering field has been limited due to this undesirable decomposition. Even with this disadvantage Al_2TiO_5 have many advantages like good wear resistance, low thermal conductivity, low thermal expansion coefficient, high thermal shock resistance, low Modulus of Elasticity, low wettability in molten metal and good chemical resistance. Another drawback of Al_2TiO_5 is its relatively low mechanical strength because of micro-cracks formation as a result of mismatch of thermal expansion along the 3-axes of the crystal lattice. In a single crystal Al_2TiO_5, expansion takes place along 2-axes and contraction along the 3rd axis on heating. Aluminum titanate is used for manufacturing of nozzles, crucibles, plungers, pouring spouts, riser tubes, thermocouples, hydraulic parts, electrical insulation and dielectric applications (sensor packaging and biochips) [4]. As the formation temperature of

Aluminum titanate is very high (≈1500°C), so we target to reduce the formation temperature using two different methods: solid-state route and solution combustion synthesis route. We also want to study the percentage decomposition of Al_2TiO_5 by calcining the samples again at 1150°C/6hr because the maximum decomposition occurs at 1100°C according to literature.

1.1 Phase diagram of Al_2O_3- TiO_2 system

$$Al_2TiO_5 => Al_2O_3 + TiO_2$$

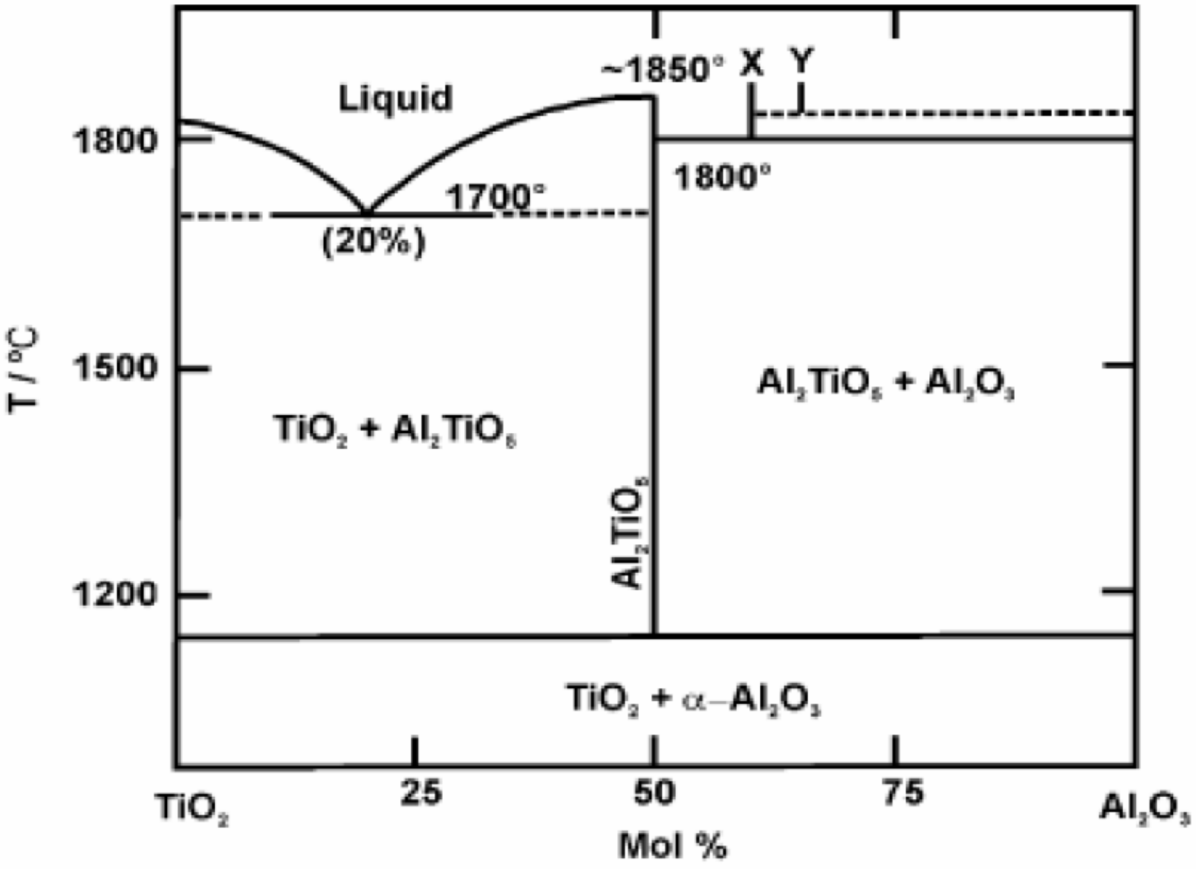
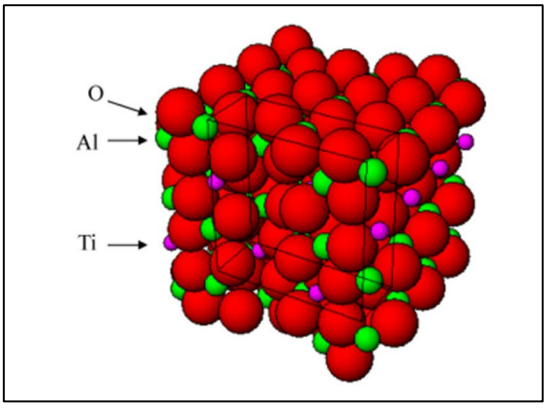
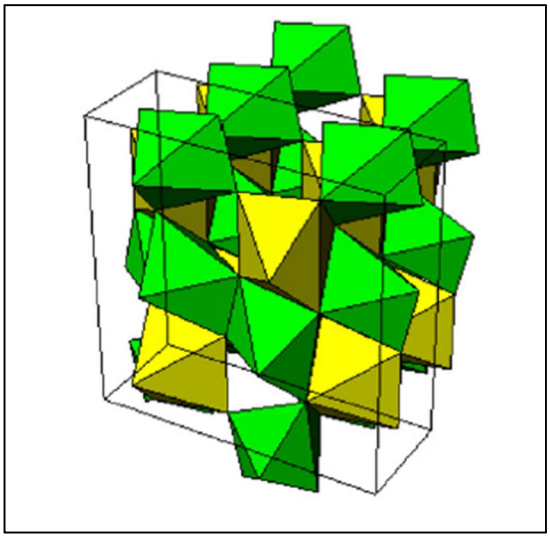


Figure 1.1: Phase diagram of Al_2O_3-TiO_2 system [5]

1.2 Structure of Al_2TiO_5



(a)



(b)

Figure 1.2: Crystal structure of Al2TiO5 showing both the (a) the oxygen–metal bonds (green: Al, purple: Ti, red: O). (b) distorted, edge-shared oxygen octahedra about each metal site [3]

2. LITERATURE REVIEW

Meybodi et al. reported microstructure and mechanical properties of Al_2O_3 -20wt% Al_2TiO_5 composite which was being prepared from alumina and titania nano-powders. In this paper, Al_2O_3-20wt% composite was being prepared from sintering of titania and alumina nano-

powders. Nano-powder was prepared by the process of ball milling and then the powders were pressed and sintered at 1300°C, 1400°C and 1500°C for 2hrs under pressure-less condition. The micro-structure and phase composition of the powders were characterized by using XRD, SEM, TEM and EDS (Energy Dispersive Spectrometer). They found that the average grain size of the composite increases with temperature. From the images obtained from SEM, it was found that there is a proper interface between Al_2TiO_5 and Al_2O_3 grains and also there is a partial distribution of Al_2TiO_5 particles in the region of grain boundary. The results obtained from XRD also showed the absence of rutile (TiO_2) in the sintered product, which implies the complete formation of Al_2TiO_5. The hardness of the samples was observed to increase as we increase the temperature (4.8, 6.2, 8.5GPa at 1300°C, 1400°C and 1500°C) [6].

Jayashankar et al. reported the effect of alumina particle size on the formation temperature of alumina-Aluminum titanate (Al_2TiO_5). Microstructure development and sintering behavior of alumina-Aluminum titanate was also studied. The alumina matrix composite constituting of 20wt% Aluminum titanate was being prepared from the powder of alumina with various average particle sizes in the range of 300-600nm. It was found that the particle size of alumina doesn`t have much effect on the temperature of formation of Al_2TiO_5, but it was found that the average grain size of alumina-Aluminum titanate increases as the particle size of alumina increases. From XRD results, it showed the absence of rutile (TiO_2) in the sintered samples which imply the complete formation of Al_2TiO_5. The experiment was done using 3 different particle sizes of alumina powder – 300nm, 450nm, 600nm, and the sintering of alumina-Aluminum titanate precursor compact was done at 1350°C with 3rs soaking time. From the DTA curve, they found that the particle size of alumina doesn`t have much effect on the temperature of formation of Al_2TiO_5 [7].

Saburo Hori et al. reported Tough corundum-Rutile composite sintered body. The effect of additives and sintering condition to improve the sinterability and microstructure were studied. The material used was corundum-Rutile composite consist of alumina of corundum phase with an alkali metal (oxide) content of 0.01 to 0.5wt% and plate shaped corundum particles whose aspect ratio is 2.5. The motive of the paper was to prepare a high toughness corundum-rutile composite. The final porosity in the toughened sample was observed to be 3%. For high toughness it was observed that the optimum value of alkali metal is 0.11 to 0.5wt% and the alumina content about 30-80wt% [8].

Ping et al. reported in situ diffraction study of self-recovery in Al_2TiO_5 (vacuum decomposed). In situ diffraction is used to characterize the self-recovery of decomposed Al2TiO5 in vacuum annealing. The reformation of Al_2TiO_5 occurred when it was heated above 1300°C. The rate of decomposition of Al_2TiO_5 was drastically enhanced in vacuum (10^{-4}tor) at 1100°C, where >90% of Al_2TiO_5 gets decomposed after only 4hrs of annealing in comparison to <10% in open atmospheric air. A similar kind of phenomenon has been observed for Al_2TiO_5 samples of various grain sizes where the phase decomposition rate increases as the grain size decreases. Starting powders used were alumina and titania. Powders were mixed using mortar, and then wet mixing was done using ethanol for 2hrs. And then the slurry was allowed to dry in an oven at the temperature of 100°C for 1 day. The dried powder was then pressed to form bar shaped samples of 20mm length and 15mm diameter. The samples were sintered at a temperature of 1400°C/1hr in open atmospheric air so as to attain a fine grained micro-structure (1-3μm) and also at 1600°C/4hrs in open atmospheric air so as to attain coarse grained (20-30μm) Al_2TiO_5. After the above process, the samples were completely decomposed by the process of annealing in a furnace at 1100°C/1hr. The furnace used in the above process was air ventilated type. It was

clearly seen that the self-recovery commences at a temperature of 1450°C through the rapid reaction of rutile and corundum in order to form Al_2TiO_5 but with a phase impurity of <40wt%. In contrast, >65wt% Al_2TiO_5 reformed for the fine grained sample and the process of self-recovery started to occur at a lower temperature i.e. at 1400°C [9].

Dumikim et al. reported Mechanical properties of Al_2TiO_5 ceramics for high temperature application. Effect of MgO as a thermodynamic stabilizer and ZrO_2 and mullite as a kinetic stabilizer on the mechanical properties of Al_2TiO_5 at high temperature was observed. Raw powders were prepared using α-Al_2O_3 and anatase. For thermodynamic stabilization, MgO additive was used and for kinetic stabilization, ZrO_2 and SiO_2 additives were used which forms secondary phase mullite at the Al_2TiO_5 grain boundary. The samples were prepared by ball milling (24hrs). The starting powders were dried (24hrs), and sieving was done. Then the dried powders were pressed at a pressure of value 1ton. After binder burnout (600°C), the samples were sintered at 1500°C, 1550°C and 1600°C for 2hrs. The bulk density and porosity were measured. Also mechanical strength at room temperature and at elevated temperature (1100°C, 1200°C and 1300°C) were measured using 3-point bending method. Results showed that the sintered density decreases with increase in sintering temperature due to the increased number of micro-cracks formed. Mullite only-AT samples had no change in microsturcture regardless of sintering temperature. The mullite only-AT sintered at 1500°C showed the highest room temperature strength (32MPa) among the samples sintered at different temperature. But in case of mix-stabilized AT, the highest strength achieved by the sample fired at 1200°C. The mechanical strength of mix-stabilized AT was higher than that of the mullite only- AT for all temperature except 1300°C. Coefficient of thermal expansion decreases with increase in sintering temperature because of an increased number of micro-cracks [10].

Segadaes et al. reported combustion synthesis of Aluminum titanate. They showed that Al_2TiO_5 can only be formed at high temperatures (endothermic reaction) because titanate being entropy stabilized. This shows the combustion synthesis of Al_2TiO_5, using the respective metal precursors - urea mixtures under short reaction timing (1min) and at low temperatures. Propellene chemistry provides the thermodynamic interpretation of the above reaction, and the morphology, grain size and specific surface area are discussed (below critical grain size, the available energy in the system is not sufficient to create micro-cracks). Al_2TiO_5 is stable only above 1280°C. It decomposes to α-Al_2O_3 and rutile below this temperature. Fast firing rates and sintering times (kept as low as 1min) showed that titanate could already be detected at a temperature of 1250°C. Increasing the sintering time, at this temperature, leads back to decomposition suggesting a metastable primary crystallization. Combustion synthesis is used to synthesize crystalline, very fine, homogeneous, unagglomerated multicomponent oxide ceramic powders without any intermediate decomposition of calcining steps. This route is exothermic in nature, and a very rapid and self-sustaining chemical reaction between metal salts and the suitable organic fuel. Aluminum titanate was prepared by the combustion reaction of $Al(NO_3)_3.9H_2O$ and $Ti[O.CH(CH_3)_2]$ urea as fuel, and NH_4NO_3 was used as combustion aid. Very fine crystalline size and homogeneity of the combustion powder might be the possible reason for the lower formation temperature of AT-phase as well as the very clean micro-structure [11].

R. Papitha et al. reported Eutectoid decomposition of Aluminum titanate (Al_2TiO_5) ceramics under Spark Plasma (SPS) and Conventional (CRH) thermal treatments. In order to observe the level of decomposition, Al_2TiO_5 specimens synthesized from the mixture of precursor oxides were heated through the processes of CRH and SPS. SPS with heating rates of

200°C per minute and 50°C per minute under 50MPa have shown phase decomposition of 95% and 74% respectively. CRH conditions resulted only in low decomposition of 11%. On thermal cycling, a substantial phase decomposition of 54% is observed. Thermo-mechanical properties conjointly correlated very well with the resulting decomposition profiles [12].

Ligia Stoica et al. reported Effect of powder precursors on reaction sintering of Aluminum titanate (Al_2TiO_5). The effect of precursor powders on the sintering of Al_2TiO_5 has been tested. Sol–gel derived powders formed by the co-gelation phenomenon, mechanical mixtures of sol–gel oxides and co-precipitated powders are also being compared. Sintering precursor powders synthesized by the process of co-gelation that has nano-size particles, under an applied electric field, lowered the temperature of formation of Aluminum titanate (Al_2TiO_5), and could achieve maximum density and minimum grain coarsening [13].

3. OBJECTIVE

The aim of our project is to synthesize Aluminum titanate (Al_2TiO_5) phase at lower temperature exploring different processing routes e.g. Solid-state route, using micron and nano-sized alumina (Al_2O_3) powder and solution combustion route and to study the stability of the solid state route prepared Al_2TiO_5 powder.

4. EXPERIMENTAL PROCEDURE

4.1 Solid State Route

Amount of TiO_2 and Al_2O_3 powders were calculated for 10gm batch preparation. The calculated powders were then weighed and transferred into a milling bottle with 20 alumina balls in it. 30ml of Isopropyl alcohol ($CH_3CHOHCH_3$, EMPLURA) was added in that bottle and pot milling for 6 hours was done. After milling, the slurry was taken out and dried under the IR lamp and grinded in mortar. Then the grinded powder was calcined in a furnace at 1350°C/4hr and 1500°C/4hr respectively.

To make pellets, one more batch of 4gms was prepared using same procedure as mentioned above. Four pellets of 0.7gms were pressed uni-axially with a load of 4ton and dwell time of 120secs. The pellets were then kept in a drier at 100°C and the next day firing was done at 1500°C/4hr. The pellets were taken out of the furnace after it was cooled to room temperature and phase identification (XRD) and microstructure (SEM) was studied.

4.2Solid State Route using nano-powders

Batch calculation was done to produce 1gm of Al_2TiO_5. We took 0.385gms of TiO_2 powder (Sigma-Aldrich) and 0.5gm of nano-Al_2O_3 powder (Reinste Nano Ventures) in a mortar and mixing was done. Then the mixture was wet mixed using propanol ($CH_3CHOHCH_3$, EMPLURA). Sufficient amount of propanol was used to wet the mixture and mixing was done until the mixture becomes dry. Again required amount of propanol was added and mixing was done. This was repeatedly done for 6-7 times. The dried powder was then calcined at temperature 1200°C/4hr, 1350°C/4hr, 1500°C/4hr. The powder was taken out of the furnace and

grinded and then phase identification (XRD) and morphology (FESEM) of the powder was studied.

To make pallets, 4gms batch of Al_2TiO_5 was calculated. 2.243gms of Al_2O_3 and 1.7567gms of TiO_2 powders were taken and mixed using the same process as mentioned above. The powder was calcined at 1350°C/4hr with a heating rate of 3°C/min. The powder was then mixed with 3wt% binder (PVA) and 4 pallets of weight 0.7gm were pressed using a load of 4ton and a dwell time of 120 secs. These pallets were kept in a drier for one night and calcined at 1500°C/4hr and then at 1150°C/6hr to study the decomposition of Al_2TiO_5 phase. After calcination phase, identification (XRD) and microstructure (FESEM) was studied.

4.3 Combustion Synthesis

Our aim is to prepare Al_2TiO_5 by solution combustion synthesis method using precursors $Al(NO_3)_3.9H_2O$, Ti-nitrate and fuel. First of all we need to make Ti-nitrate solution.

To prepare the solution we need following materials:

- Ammonium sulphate ($(NH_4)_2SO_4$)
- Sulphuric acid (H_2SO_4)
- Titania powder (TiO_2)
- Ammonium hydroxide (NH_4OH)
- Nitric acid (HNO_3)
- DI water

Our first step is to add 80gms of Ammonium sulphate ($(NH_4)_2SO_4$, Merck) into 200ml of Sulphuric acid (H_2SO_4, Merck) in a beaker while heating (100°C) and constant stirring. The

solution is stirred until the solution is clear. After we get the clear solution, 10gms of Titanium oxide (TiO_2, Sigma-Aldrich) is slowly added into the beaker. Constant stirring is required; otherwise the TiO_2 powder will not dissolve in the solution completely. After getting a clear solution, heating is being stopped, and the beaker is kept in the fume-hood to cool at room temperature. When the solution is completely cooled at room temperature, water is added in 1:3 ratio in an ice-bath condition. Here also stirring is required. Again we will get a clear solution and in that solution, ammonia solution (NH_4OH, Merck, 30%GR) is slowly added in an ice-bath condition to maintain its pH10. At pH10, the solution will form a white color precipitate (Titanium hydroxide). We need to reduce the pH to 7 by washing the precipitate using DI water. Then the precipitate is filtered using handmade filter papers and then dissolved in nitric acid (1:2) to form clear solution of Titanium ions. The strength of the solution is measured by again taking the precipitate in a platinum crucible and firing it at 950°C/1hr. The titanium nitrate solution was kept in a refrigerator.

The flow chart to prepare Titanium-nitrate solution is given below:

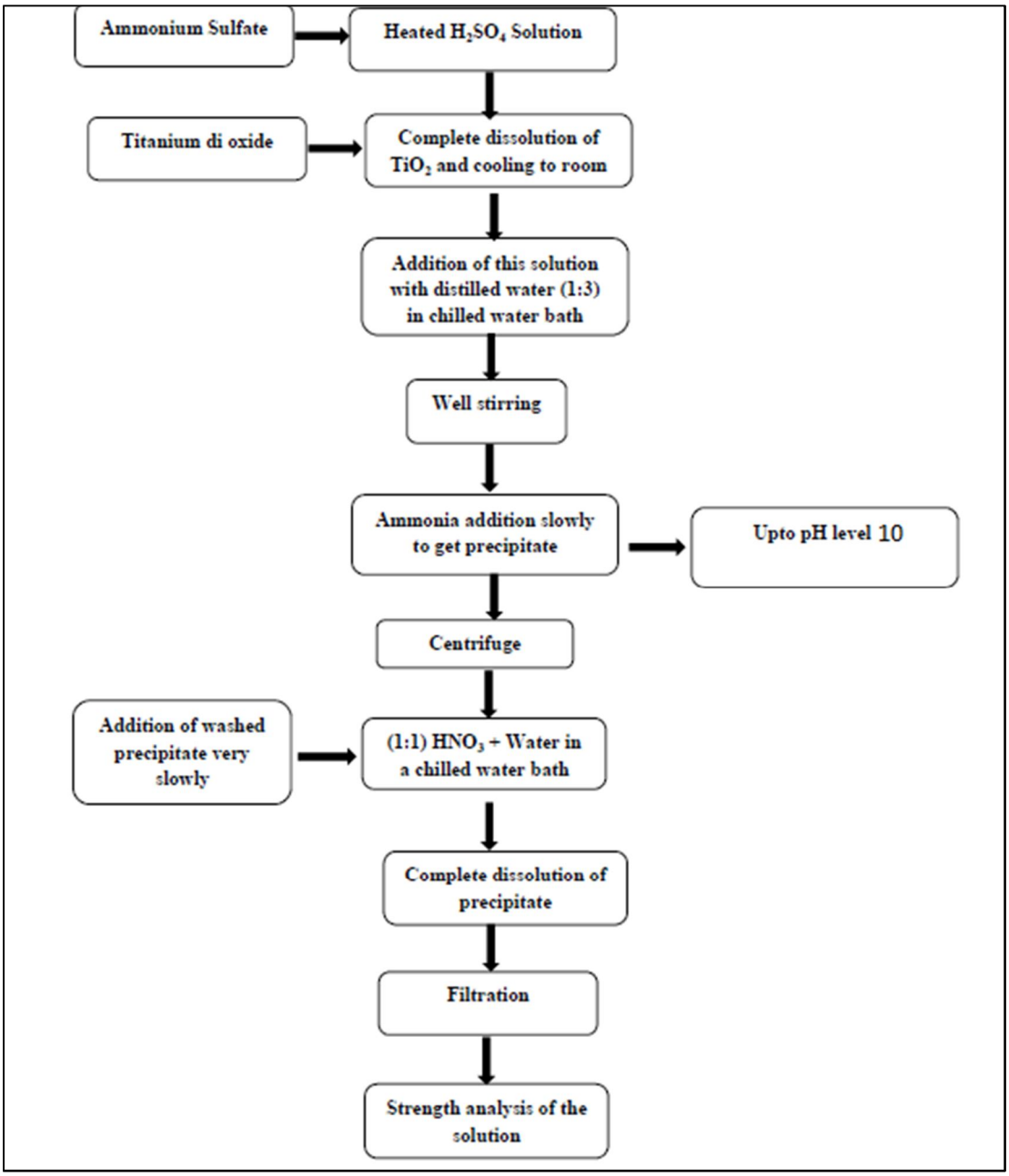


Figure4.1: Flow chart for preparation of titanium nitrate solution

Reactions in preparation of Ti-nitrate solution:

$$TiO_2 + H_2SO_4 \Rightarrow TiO(SO_4) + H_2O$$

$$TiO(SO_4) + 2NH_4OH \Rightarrow TiO(OH)_2 \downarrow + (NH_4)_2SO_4$$

$$TiO(OH)_2 + 2HNO_3 \Rightarrow TiO(NO_3)_2 + 2H_2O$$

First batch was prepared using citric acid as fuel by varying the the molar ratio of metal (Al:Ti) and citric acid to get a uniform and complete combustion. Three different metal (Al:Ti) and citric acid ratio were studied 2:1:2.22, 2:1:4.44 and 2:1:8. 50ml of $TiO(NO_3)_2$ solution was taken in a 500ml beaker and slowly $Al(NO_3)_3.9H_2O$ was added while heating the beaker on a hot plate at 100°C and 400RPM and then citric acid was added. After half-an hour the temperature was slowly increased to 250°C. After 2-3hrs the solution forms a white viscous gel and the gel will change into a black-brown colored gel. This gel is collected for DSC-TG characterization. Within 2-3 minutes this black colored gel will convert into a light weighed mass. The beaker is then constantly heated for 1 hour. The powder is then collected and calcined at different temperature 1200°C, 1350°C and 1500°C for 4 hours with a heating rate of 3°C/min. After calcination the phase identification is studied by XRD and the particle size morphology was studied using SEM.

4.4 Characterization

4.4.1 X-Ray Diffraction Studies

X-Ray Diffraction machine is used to characterize materials for the following information such as phase analysis (crystalline phase/ non-crystalline phase inter-metallic/ elemental phase), orientation analysis, strain determination, lattice parameter determination and order-disorder transformation. A X-ray diffractometer (Rigaku Japan/Ultima -IV) (using a nickel filtered Cu K_α radiation) was employed to analyze the samples formed by simple solid-state route and combustion synthesis route. The scanning range of 2θ was from 15°-60° with a scanning speed of 20°/minute. X-pert high score software was used to analyze the phase to identify different types of phases.

4.4.2 Field Emission Scanning Electron Microscope (FE-SEM)

The FESEM is a type of electron microscope in which the specimen placed is directed by high energy beam of electrons. It is used to produce 2D-image of a specimen of any size or thickness. This device has a hot filament to generate high energy electrons, which are further accelerated by a series of magnetic and electric fields thus interacting with the sample. When these electrons interact with the sample, they produce signals which contain Intel about the properties of the sample such as composition, surface or near surface topography, etc. It is primarily employed to investigate the microstructure of bulk specimens. It can produce 2D images of very high resolution which can give information about <1nm in size. The magnification range of conventional SEM is 10x – 200,000x with spatial resolution of 50 – 100 nm which makes it possible to scan areas which vary from 1cm-5μm in width. The signals produced by a SEM include back scattered electrons, secondary electrons, light

(cathodoluminescence), characteristic X-ray, etc. Secondary electron imaging is used in case of SEM micrographs.

5. RESULTS AND DISCUSSION

5.1 Solid State Route

5.1.1 XRD Analysis

Figure 5.1 shows XRD pattern of powder prepared using coarse Al_2O_3 (average eparticle size of 10 μm) and TiO_2 of particle size (average eparticle size of 150 nm) and calcined at 1350°C and 1500°C.

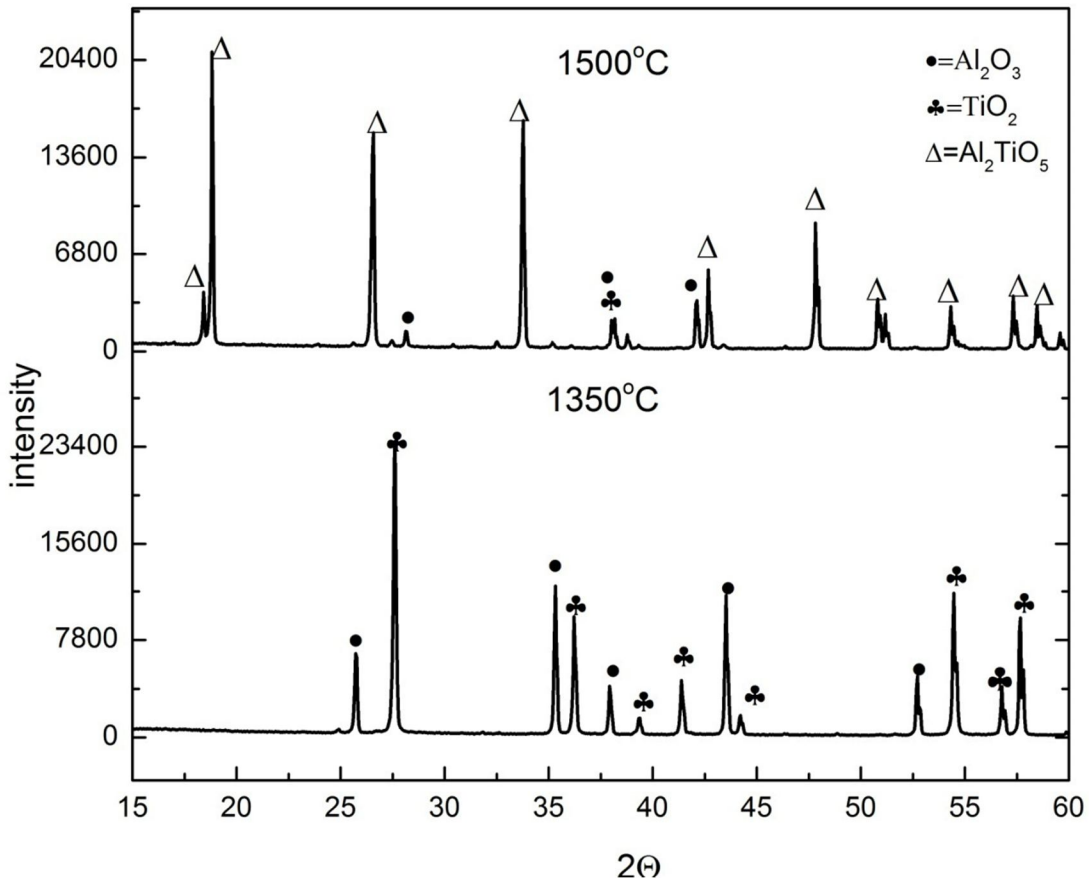
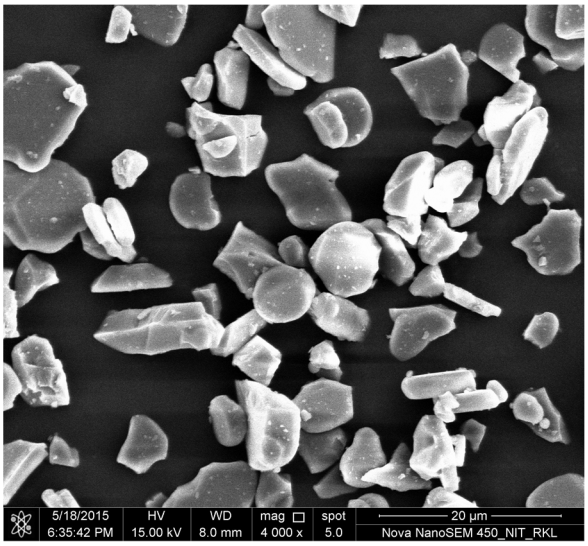


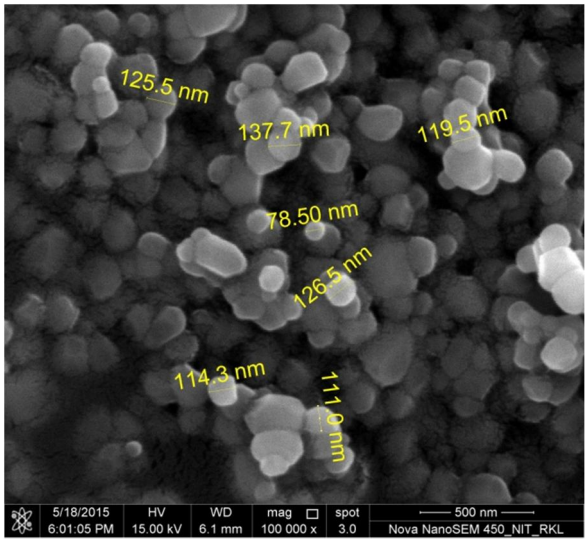
Figure 5.1: XRD graph for samples calcined at 1350°C/4h and 1500°C/4hr

From the XRD pattern, it is concluded that 97% of Al_2TiO_5 phase was formed in the samples calcined at 1500°C/4hr. No AT phase was detected in samples calcined at 1350°C/4hr.

5.1.2 Microstructural Analysis



(a)



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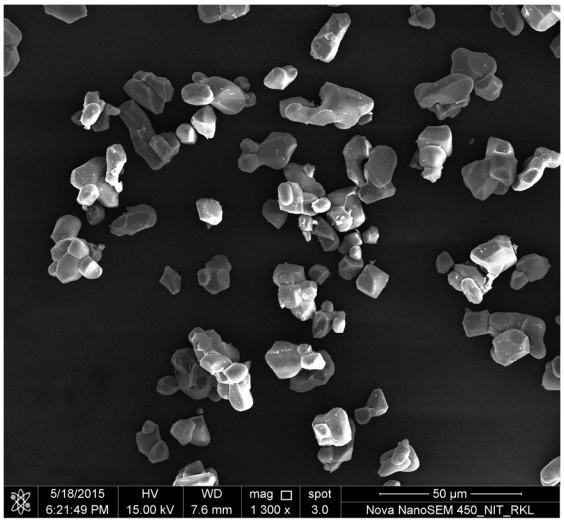


(c)

Figure 5.2: FESEM micrographs of (a) Alumina powder, (b) Titania powder (c) Sample calcined at 1500°C/4hr

Figure 5.2 shows FESEM micrograph of different powder samples. From the micrograph, it is observed that the average particle size of Al_2O_3 was 10 µm with plate like morphology. TiO_2 powders are spherical in shape with a average particle size of 150 nm. AT phase has irregular to cuboidal morphology with particle sze around 11µm.

5.2Solid-State Route Using Al_2O_3-Nano Particles

5.2.1 XRD Analysis

Figure 5.3 shows XRD pattern of Al_2TiO_5 prepared using nano-Al_2O_3 (Reinete) particles of size 30-90nm and TiO_2 of particle size(150 nm) and calcined at 1200°C, 1350°C and 1500°C.

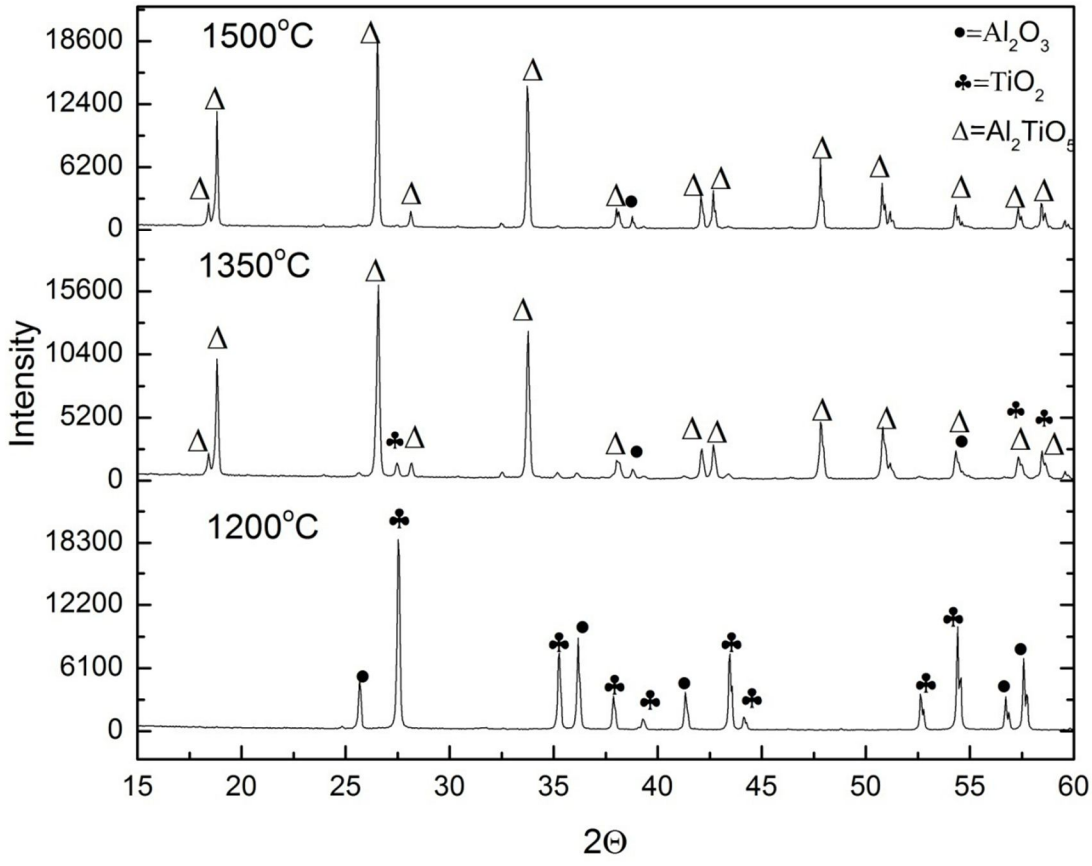
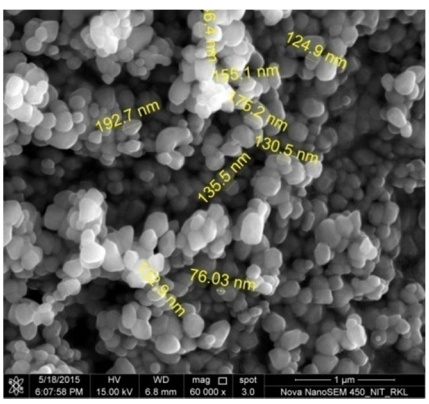


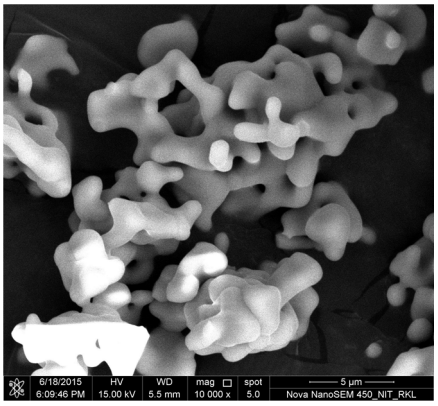
Figure 5.3: XRD patterns of samples calcined at 1200°C, 1350°C and 1500°C/4hr

No AT phase was formed in sample calcined at 1200°C/4hr. But 91% and 98.9% AT phase was formed in sample calcined at 1350°C/4hr and 1500°C/4hr respectively. It reveals that the formation temperature of Al_2TiO_5 decreases as we reduce the particle size of starting powder (here nano-alumina).

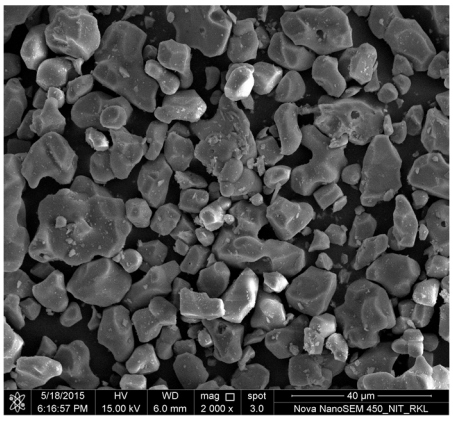
5.2.2 Microstructure Analysis



(a)



(b)



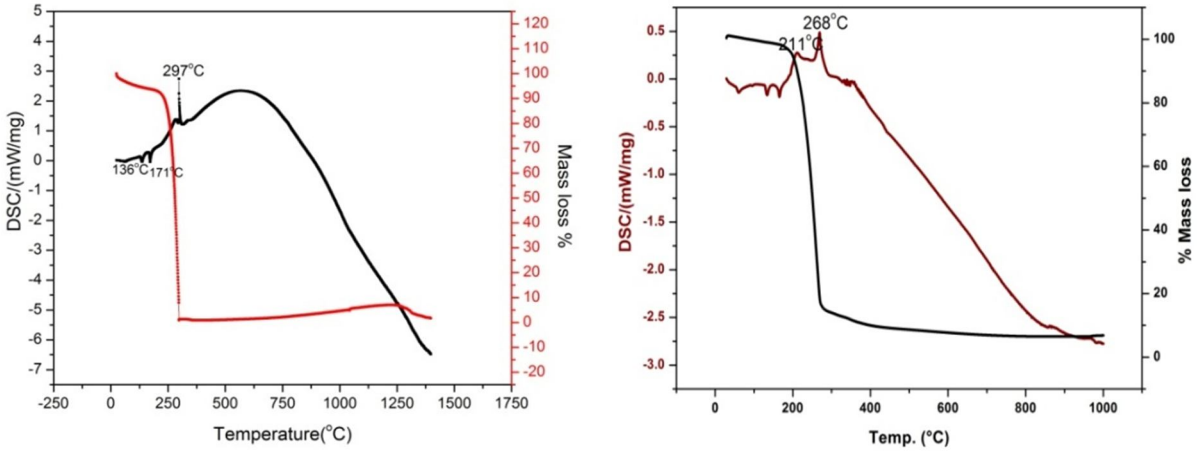
(c)

Figure 5.4: FE-SEM micrograph of samples calcined at 1200°C (a), 1350°C (b) and 1500°C (c)/4hrs

Figure 5.4 shows the FESEM micrograph of samples calcined at 1200°C, 1350°C and 1500°C/4hrs. Samples calcined at 1200°C shows an average grain size of 170 nm and spherical shape of particles were observed, but in case of samples calcined at 1350°C/4hrs, cylindrical, elongated and interconnected particles were observed with a grain size of 2µm. Samples calcined at 1500°C/4hrs showed irregular shaped particles and the grain size was found 10µm.

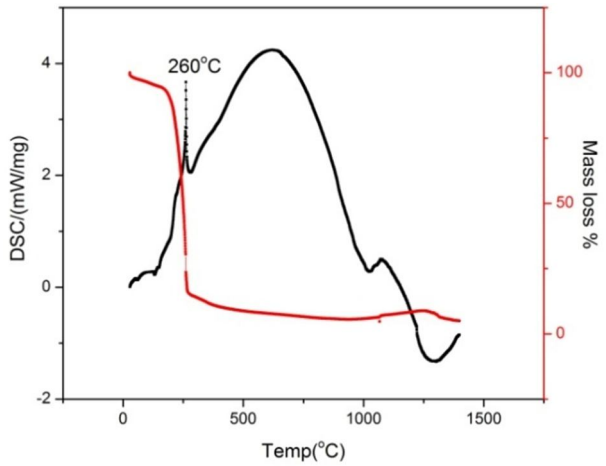
5.3 Solution Combustion Synthesis Route

5.3.1 Thermal Analysis



(a)

(b)



(c)

Figure 5.5: shows DSC-TG of AL_2TiO_5 using citric acid as a fuel in a molar ratio of (a) 2:1:2.22, (b) 2:1:4.44 and (c) 2:1:8

From figure 5.5 (a), It shows endothermic peaks at 136°C and 171°C, corresponds to dehydration of adsorbed water, which leads to a weight loss of 10%. The exothermic peak at 297^{o}C corresponds to the decomposition of the metal complex, pyrolysis of organic groups and oxide phase formation, resulting in weight loss of 75%. The weight loss beyond 297^{o}C was negligible. It shows highly exothermic and single stage decomposition. Instantaneous rise in temperature and sharpness of the weight change of TG plot indicates a self-propagating type autocombustion reaction. It was observed that with increase in citric acid content exothermic peak temperature decreases.

5.3.2Phase Analysis

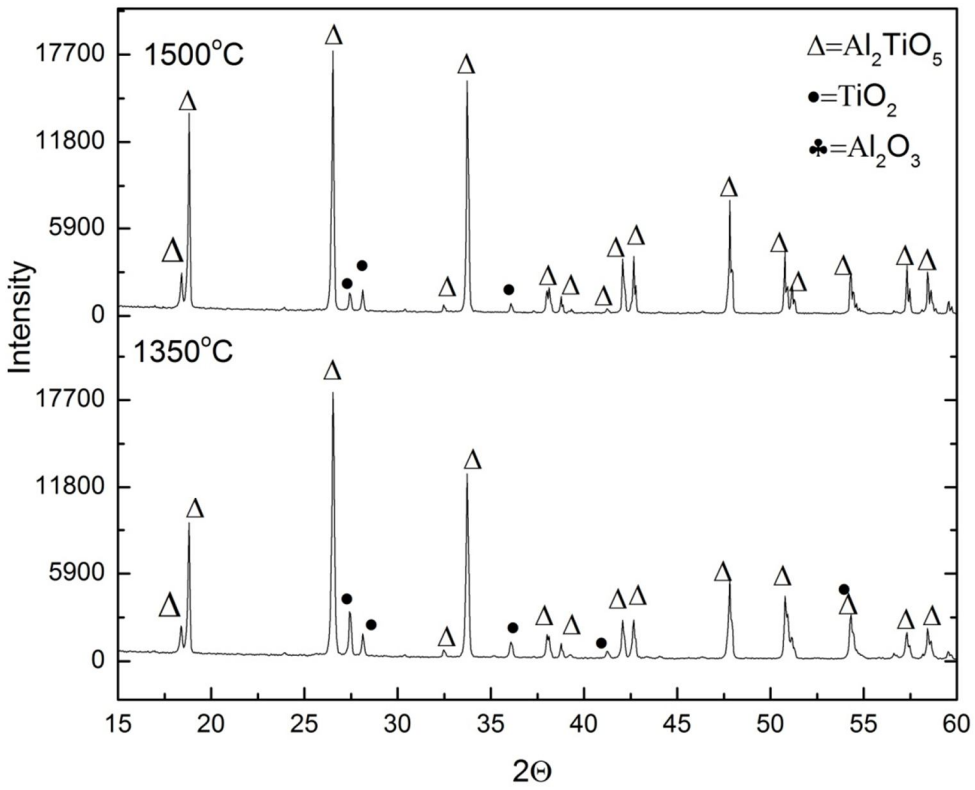


Figure 5.6: XRD pattern of sample using citric acid as fuel in a molar ratio 2:1:4.44 and calcined at 1350°C/4hr and 1500°C/4hr

It was found that Al_2TiO_5 phase was not fromed in samples calcined at 1250°C/4hr, only Al_2O_3 and TiO_2 unreacted phase were observed (not shon in XRD). Using citric acid as a fuel in ratio 2:1:4.44 in combustion synthesis of Al_2TiO_5 and calcining it at 1350°C/4hr and 1500°C/4hr gives 92% and 96% Al_2TiO_5 phase, respectively. The amount of unreacted Al_2O_3 and TiO_2 are less in comparison to samples synthesized using solid state route at 1350°C.

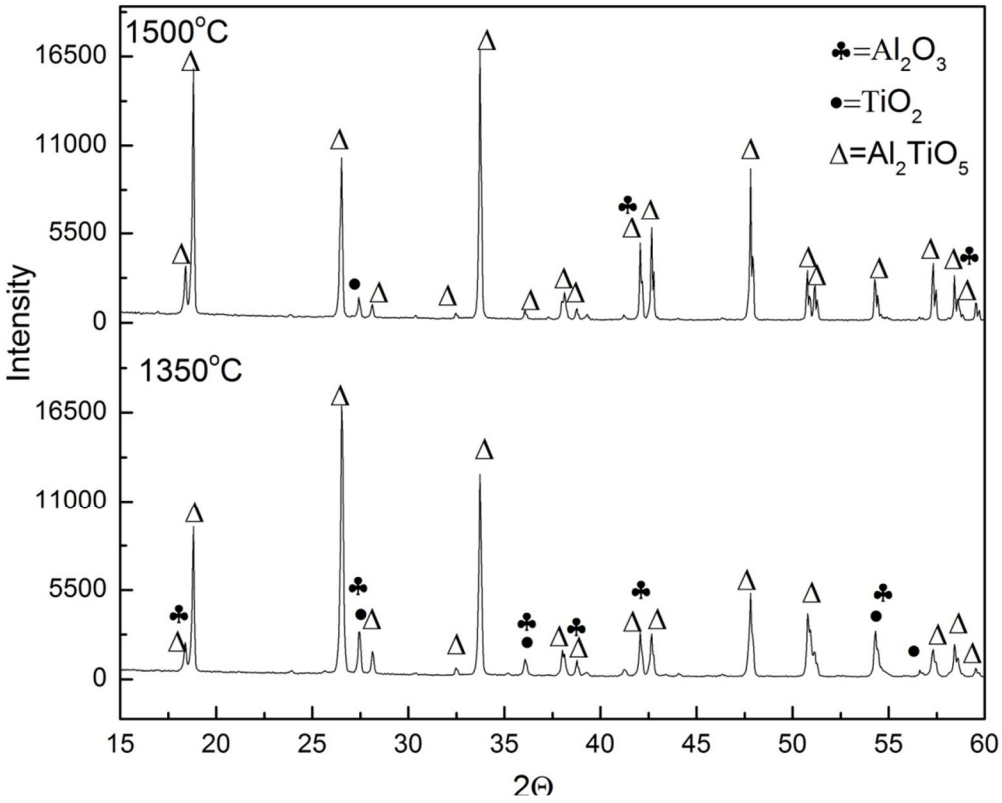


Figure 5.7: XRD pattern of sample using citric acid as fuel in a molar ratio 2:1:8 and calcined at 1350°C/4hr and 1500°C/4hr

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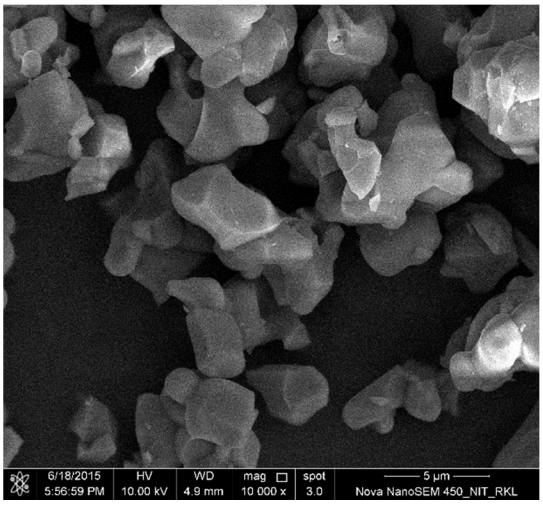
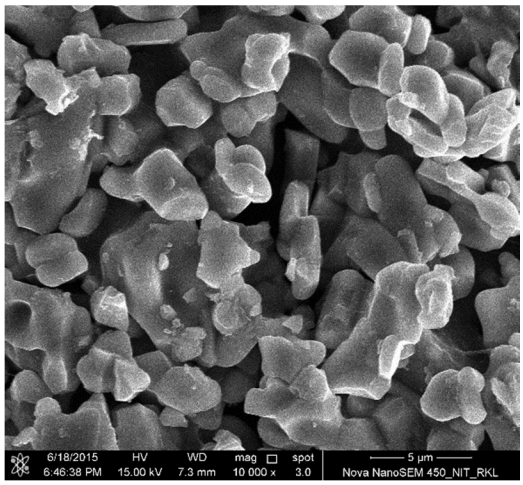
Using citric acid as a fuel in ratio 2:1:8 in combustion synthesis of Al_2TiO_5 and calcining it at 1350°C/4hr and 1500°C/4hr gives 93% and 94% Al_2TiO_5 phase respectively.

5.3.3 FE-SEM Analysis



(a)



(b)

Figure 5.8: FE-SEM micrograph of sample prepared through combustion route

(a) citric acid used as fuel in molar ratio 2:1:4.44 and calcined at 1350°C
(b) citric acid used as fuel in molar ratio 2:1:8 and calcined at 1350°C

From the FESEM micrograph, it was observed that the particles are agglomerated and irregular in shapes with an average particle size of 3µm(0.9-4.5µm),

5.4 Phase Stabilty of Solid state route prepared Al_2TiO_5

5.4.1 Phase Analysis

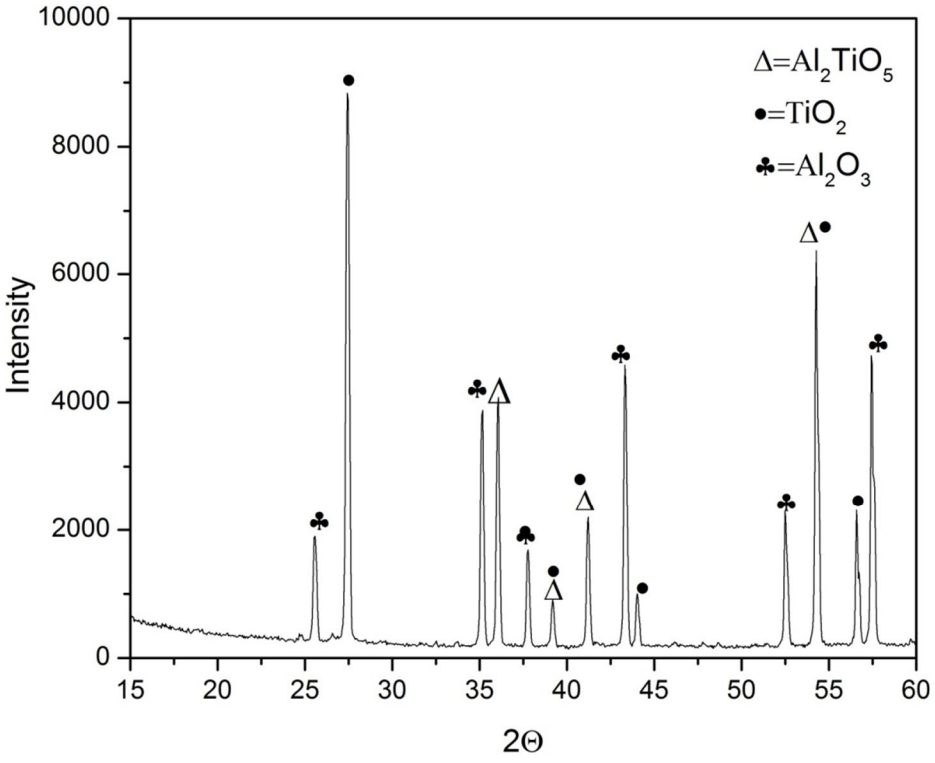


Figure 5.9: XRD graph for sample (pellet) calcined at 1500°C/4hr and then 1150°C/4hr.

Figure 5.9 shows XRD graph for samples (pellet) fired at 1500°C/4hr and then 1150°C/6hr. It was observed from the above graph that 40% of aluminum titanate phase was retained when compared to 97%AT formed at 1500°C.

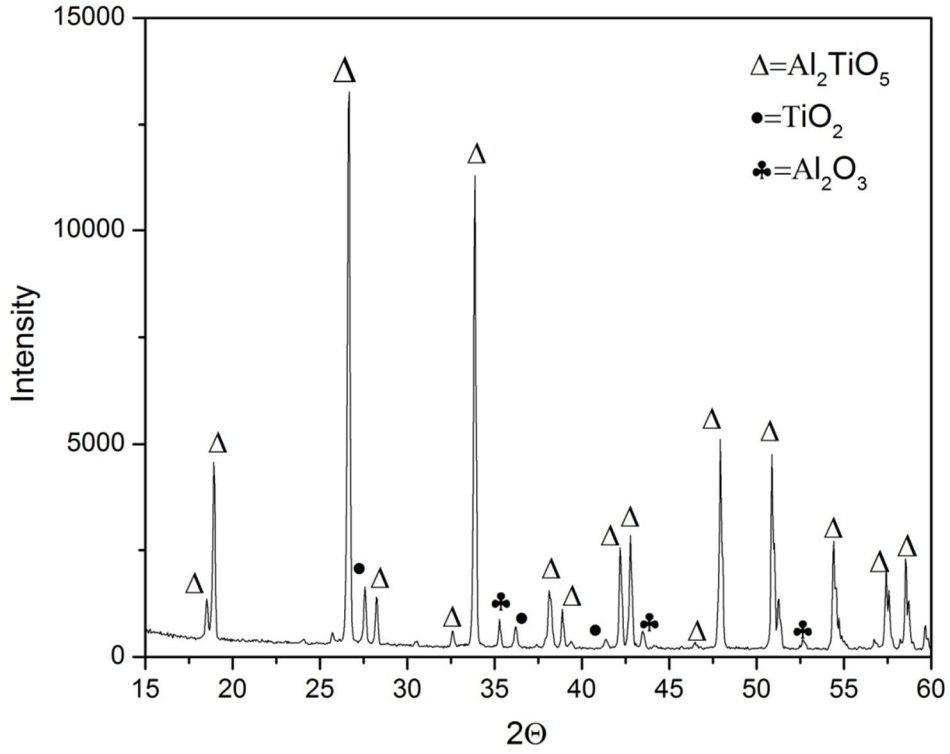


Figure5.10: XRD graph for sample (pallet containing nano alumina) calcined at 1500°C/4hr and then at 1150°C/4hr

Figure5.10 shows XRD graph for sample (pallet) calcined at 1500°C/4hr and then at 1150°C/6hr. 93% Aluminum titanate phase was retained (only 5% decomposition of AT phase) compared to %AT (98%) phase in samples calcined at 1500°C/4hrs.

5.4.2 FE-SEM Analysis

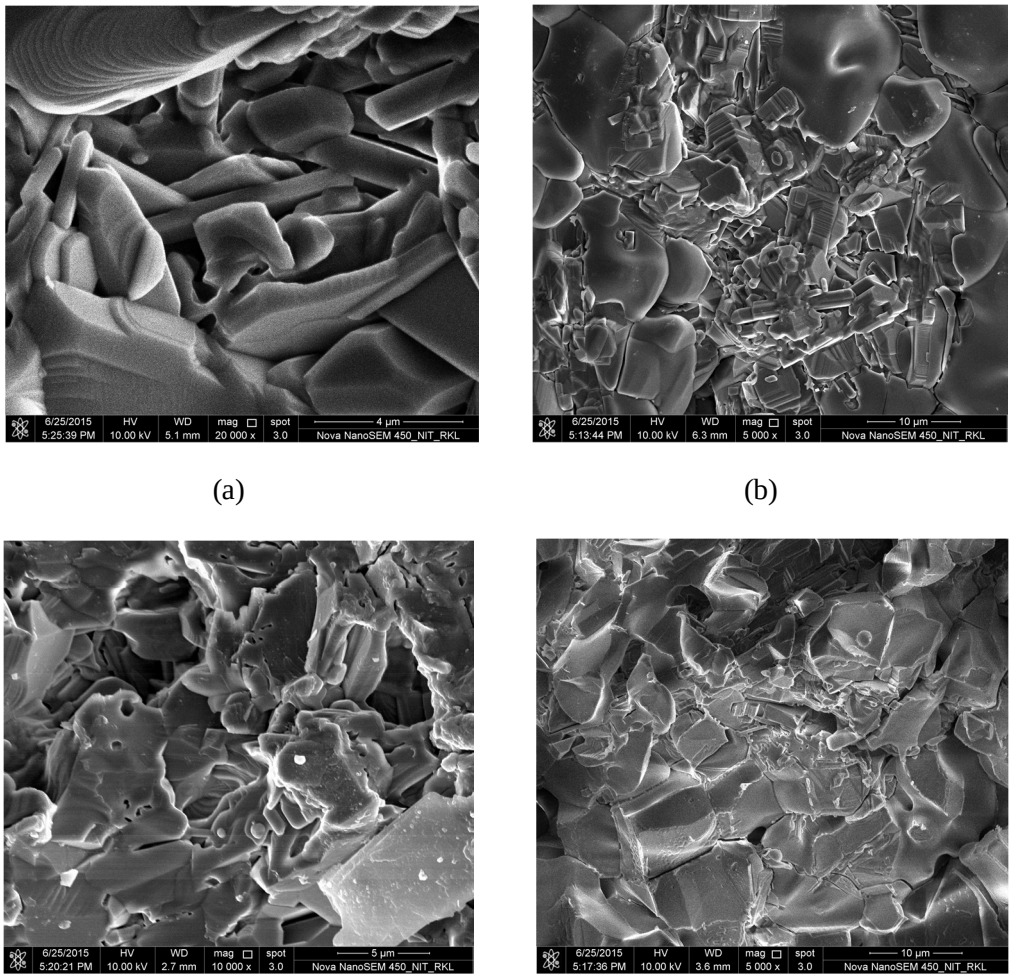


Figure 5.11: Microstructure of pellets fired at 1150°C/6hr
(a)micron size alumina containing pellet (as fired), (b) nano-size Alumina containing pellet (as fired) (c) and (d) fracture surfaces of the same samples respectively

Figure 5.11 shows the microstructure of pellets (micron size and nano size Alumina both) calcined at 1500℃/4hr and then 1150℃/6hr. Plate shaped particles were observed in pellets in which micron size alumina was used but in case of nano-alumina containing pellets, the particles are interconnected which proves that there is less decomposition of AT-phase than samples prepared using micron size alumina.

6. CONCLUSION

- The formation temperature of Aluminum titanate can be reduced (1350°C) by using nano-sized precursors (here nano alumina used).
- Solution combustion synthesis route is also helpful to reduce the formation temperature compared to solid-state route, but the purity of the phase is less at 1350° compared to samples prepared through solid-state route using nano alumina.
- Aluminum titanate prepared using nano-alumina showed very less percentage decomposition (5%) of AT phase on thermal cycling than micron size alumina made samples (approx 57%).

7. References

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